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STRUCTURE OF 4-METHYLPYRIDINIUM HYDROGEN SULFIDE

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SUMMARY

4-Methylpyridinium hydrogen sulfide, $[\text{C}_6\text{H}_7\text{NH}]\text{HS}$, $M_r = 127.21$, consists of $\text{C}_6\text{H}_7\text{NH}^+$ cations and HS^- anions. $Z = 2$ for the crystal with monoclinic space group Cm (#8), dimensions of $a = 8.679$ (2) Å, $b = 7.964$ (1) Å and $c = 4.860$ (2) Å, an angle β of $101.10(2)^\circ$, and a volume of $V = 329.6(3)$ Å³. $R = 0.039$ and $R_w = 0.048$ for 385 reflections with $F_o^2 > 3\sigma(F_o^2)$ and 59 variables. Both the $\text{C}_6\text{H}_7\text{NH}^+$ cation and the HS^- anion lie on crystallographic mirror planes with the N, S, two carbon atoms and two hydrogen atoms positioned in the planes. The hydrogen atom of the HS^- anion was not located.

EXPERIMENTAL

The 4-Methylpyridinium hydrogen sulfide, also known as γ -picolinium hydrogen sulfide, was obtained as a by product of the reaction between GaCl_3 and thioglycolic acid ($\text{HSCH}_2\text{CO}_2\text{H}$) in a γ -picoline solution. The specifics of the reaction, which was carried out under an argon atmosphere, are as follows. 2.0mL (28.7mmol) of $\text{HSCH}_2\text{CO}_2\text{H}$ was slowly added to a solution of 0.87g of GaCl_3 in 30mL of γ -picoline. After reacting for 24 hours, the precipitate which formed was removed by filtration. The filtrate solution was layered with 30mL of freshly distilled hexanes. This produced colorless crystals of the 4-methylpyridinium hydrogen sulfide which were allowed 80 days to grow. The crystals were then collected, washed with three 10mL aliquots of hexanes and dried in vacuo.

A $0.47 \times 0.32 \times 0.22$ mm crystal was sealed in a glass capillary and mounted on an Enraf-Nonius CAD-4 automated diffractometer which utilizes Mo $K\alpha$ radiation of wavelength $\lambda = 0.71073$ Å. Cell constants were determined from least-squares refinement of 25 reflections in the range $18 < \theta < 23^\circ$. Intensity data were collected using the ω - 2θ scan technique in the range $4 < 2\theta < 55^\circ$ at a temperature of 20°C . The scan rate varied from 2 to $16^\circ \text{ min}^{-1}$ with ω -scan width = $(0.74 + 0.350 \tan \theta)$. Intensities were corrected for Lorentz and polarization effects. Absorption effects were corrected based on the empirical method of Walker & Stuart (ref. 12) with $T_{\min} = 0.421$ and $T_{\max} = 1.000$. 413 unique reflections were collected in the index ranges $0 \leq h \leq 11$, $0 \leq k \leq 10$, and $-6 \leq l \leq 6$. Of these unique reflections, the 385 whose intensities fit $F_o^2 > 3\sigma(F_o^2)$ were used in the refinements. The structure was solved using the structure solution program SHELX-86 (ref. 10). The remaining atoms were located in succeeding difference Fourier syntheses. With the exception of the hydrogen

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atom of the HS⁻ ion, hydrogen atoms were located and their positions and isotropic thermal parameters were refined. The structure was refined in full-matrix least squares. The function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight, w , defined by the Killean and Lawrence (ref. 8) method with terms of 0.020 and 0.1. The final refinement parameters are $R = 0.039$, $R_w = 0.048$, $S = 1.617$ and $(\Delta/\sigma)_{\max} = 0.02$. The maximum residual peak in the final difference Fourier map was $0.25 \text{ e}\text{\AA}^{-3}$. Atomic scattering factors were taken from reference 3. Anomalous dispersion effects were included in F_c (ref. 6) and the values of f' and f'' were those of reference 4. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends. All calculations were performed on a VAX computer. Refinement was done using Enraf-Nonius *MolEN* (ref. 5). Table I* lists final positional and equivalent isotropic thermal parameters. Bond distances and angles are listed in Table II. The *ORTEP* (ref. 7) drawing in Figure 1 shows the stereochemistry of the molecule.

RELATED LITERATURE

X-Ray structural characterizations of 4-methylpyridinium bromide (ref. 2) and piperidinium hydrogen sulfide (refs. 1 and 11). ¹H NMR spectrum and viscosity and conductance measurements of 4-methylpyridinium bromide (ref. 9).

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*Lists of structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH 1 2HU, England.

TABLE I.—POSITIONAL AND EQUIVALENT ISOTROPIC
THERMAL PARAMETERS WITH e.s.d.'s IN PARENTHESES

$$B_{eq} = (1/3) \sum_i \sum_j B_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
S	0.16570	1.	0.95320	3.86(2)
N	0.4327(5)	1.	0.6516(9)	3.61(8)
C(2)	0.4863(5)	0.8540(5)	0.5731(9)	3.93(7)
C(3)	0.5969(5)	0.8508(5)	0.4101(8)	3.72(6)
C(4)	0.6555(6)	1.	0.323(1)	3.23(8)
C(7)	0.7805(7)	1.	0.152(1)	4.8(1)
H(1)	0.349(9)	1.	0.77(2)	6(2)*
H(21)	0.459(7)	0.756(9)	0.68(1)	8(2)*
H(31)	0.632(8)	0.754(9)	0.35(1)	9(2)*
H(71)	0.872(9)	1.	0.30(2)	6(2)*
H(72)	0.77(1)	0.89(1)	0.01(2)	12(2)*

*Refined with isotropic B's.

TABLE II
[Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses.]

S-H(1)	1.98(9)	C(3)-C(4)	1.390(5)
N-C(2)	1.335(5)	C(3)-H(31)	0.90(8)
N-H(1)	1.00(9)	C(4)-C(7)	1.488(8)
C(2)-C(3)	1.357(7)	C(7)-H(71)	1.0(1)
C(2)-H(21)	0.98(8)	C(7)-H(72)	1.1(1)
C(2)-N-C(2)	121.1(6)	C(3)-C(4)-C(7)	121.2(3)
C(2)-N-H(1)	119.4(3)	C(4)-C(7)-H(71)	99(6)
N-C(2)-C(3)	120.5(4)	C(4)-C(7)-H(72)	113(5)
N-C(2)-H(21)	114(4)	C(4)-C(7)-H(72)	113(5)
C(3)-C(2)-H(21)	124(4)	H(71)-C(7)-H(72)	115(6)
C(2)-C(3)-C(4)	120.2(4)	H(71)-C(7)-H(72)	115(6)
C(2)-C(3)-H(31)	121(5)	H(72)-C(7)-H(72)	103(11)
C(4)-C(3)-H(31)	118(5)	S-H(1)-N	173(8)
C(3)-C(4)-C(3)	117.5(5)		

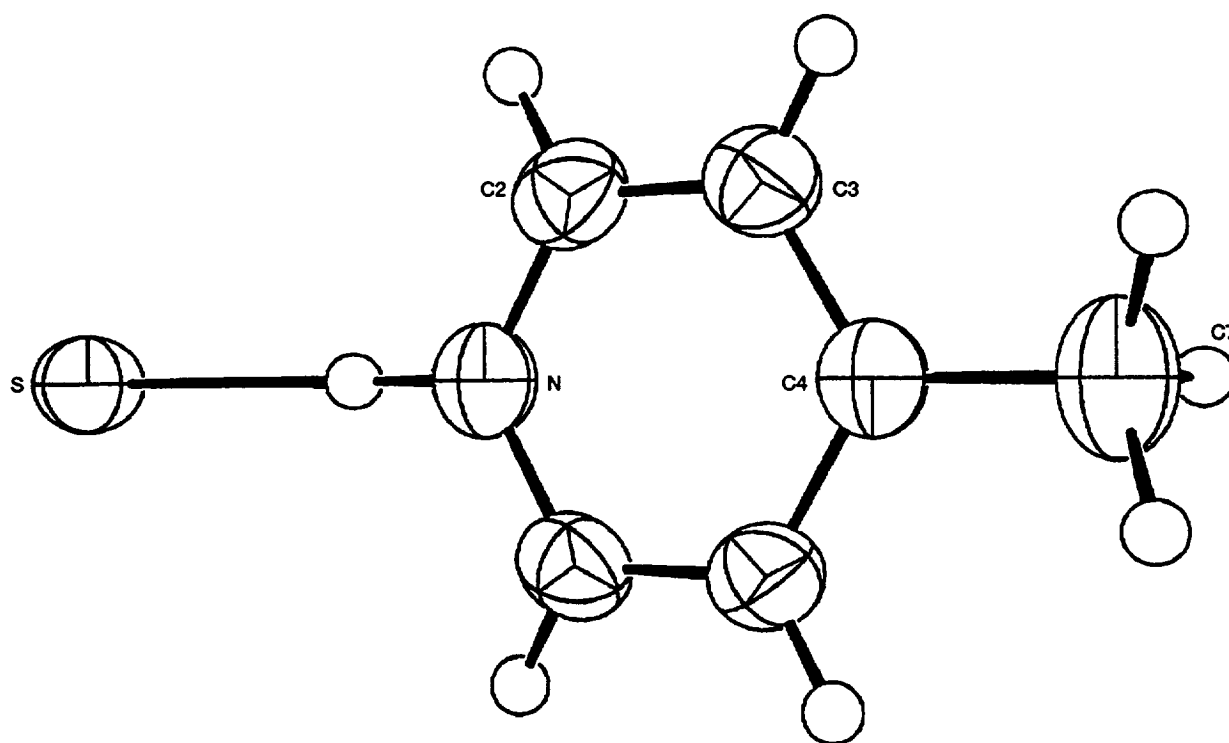


Figure 1.—ORTEP (Johnson, 1965) drawing of the [C₆H₇NH][HS] molecule (without the undetected H of HS⁻) showing the atomic-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level while isotropic hydrogen thermal parameters are represented by spheres of arbitrary size.

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